SYNTHETIC LUBRICANT

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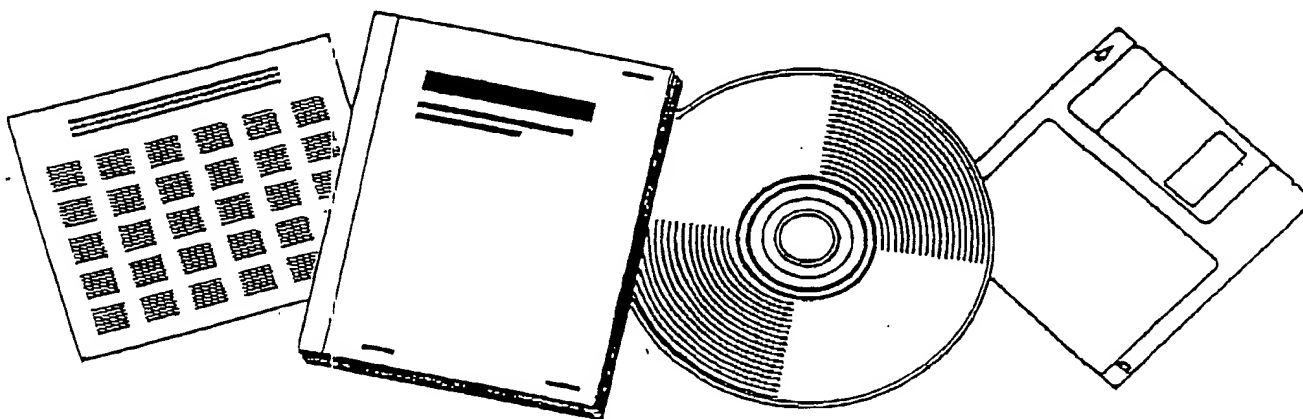
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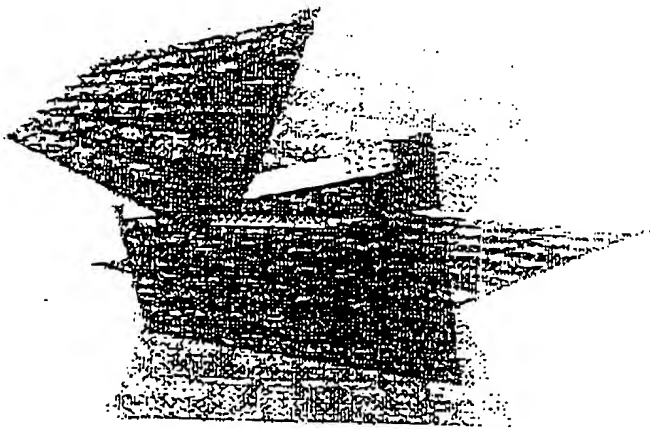
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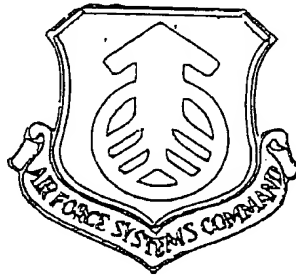SRIM® requires an NTIS Deposit Account. The NTIS employee you speak to will help you set up this account if you don't already have one.

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FOREIGN TECHNOLOGY DIVISION

SYNTHETIC LUBRICANT

by

S. S. Al'tman, A. A. Myshalova, et al.

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EDITED TRANSLATION

SYNTHETIC LUBRICANT

By: S. S. Al'tman, A. A. Myshalova, et al.

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ABSTRACT

(U)   This Author Certificate introduces a synthetic oil made from pentaerythritol ester and synthetic fatty acids. To insure the efficiency of the synthetic oil in refrigeration machines running on freon-22, use of the synthetic fatty acid with 5--9 atoms of carbon and antioxidant additive is suggested. Use of ionol in an amount of 0.5--1.0 wt percent or parahydroxydiphenylamine in an amount of 0.3--0.5 wt percent is recommended.

SYNTHETIC LUBRICANT

S. S. Al'tman, A. A. Myshalova, K. D. Kan, and L. G. Gorda

The invention is concerned with the composition of a synthetic lubricating oil to be applied in the field of refrigeration equipment construction, in particular for the lubrication of refrigerator compressors operating on Freon-22 at temperatures down to minus 80°C.

Ordinarily mark KhF-22 petroleum oil, per GOST 5546-59, is used to lubricate such machinery. Lubrication with petroleum oils cannot ensure normal reliable operation of refrigerator compressors operating on Freon-22 at a temperature down to minus 80°C, since drops of KhF-22 oil which fall onto the evaporation section can harden and clog up the system; this reduces the possibility of obtaining low temperatures on the order of minus 70 or minus 80°C.

For refrigerator lubrication it is proposed to utilize complex esters of neopentyl alcohols and C_5-C_9 fatty acids, which will form solutions with Freon-22 which do not congeal at a temperature of minus 80°C, since these esters have a significantly higher pour point and can therefore ensure normal operation of refrigerator compressors utilizing Freon-22. The proposed synthetic refrigerating oil (mark LZ-KhF-22S) is a complex ester, stabilized by the antioxidant additives para-oxydiphenyl amine or Ionol, obtained by the interaction of pentaerythrite and synthetic fatty acids with 5-9 carbon atoms in the chain.

For example (wt. %):

Pentaerythrite ester	99.5-99.7
Para-oxydiphenyl amine	0.5-0.3
Pentaerythrite ester	99.0-99.5
Ionol	1.0-0.5

Object of the Invention

1. The synthetic oil based on the complex ester of pentaerythrite and SZhK is distinguished by the fact that to ensure operational effectiveness of the oil in refrigerating machines operating on Freon-22, synthetic fatty acids with 5-9 carbon atoms and an antioxidant additive are introduced into it.

2. The oil in paragraph 1 is further distinguished by the fact that Ionol (0.5-1.0 wt. %) or para-oxydiphenyl amine (0.3-0.5 wt. %) is used as the antioxidant additive.

Organization	No. Cys.	Organization	No. Cys
AIR FORCE		**OTHER DOD AGENCIES**	
Hq USAF			
AFCRL (CRXLR)	1	DDC	20
ARL (ARB) WP, AFB	1	C205 Army Map Service	1
AWS (AWVAS)	1	C513 Picatinny Arsenal	1
Hq AFSC		C523 Harry Diamond Lab	1
AFETR (ETW)	1	C535 Aviation Mat Comd	1
ASD (ASFS)	9	C591 U.S. Army (FSTC)	3
SAMSO (SMFA)	1	C619 MID Redstone	1
FTD		C663 Army Security Agency	1
TDBAE	3	D153 Pac Msl Range	1
ATD (2)		H521 Hq USAREUR - UTIC	1
PHS (1)		CC72 CDC INLAND COMBAT	1
TDBAS-2	10	C525 ABERDEEN PC	1
TDBID-2	2	U.S. Navy (STIC/N2E)	1
TDBR	1		
TDCS	1		
Det #3 (FTD)	2		
TDP (PHE)	2	**OTHER GOVERNMENT AGENCIES**	
PAD (1)			
PRB (1)		AEC (Tenn)	2
TDPTA	3	AEC (Wash)	2
PTA4G (1)		NASA (ATSS-T)	1
PTA4H (1)			
PTA4R (1)			

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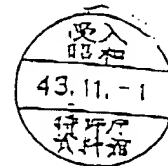
Авторы изобретения: С. С. Альтман, А. А. Мышалова, К. Д. Кан и Л. Г. Горда

Заявитель: Ленинградский опытный нефтемаслозавод им. Шаумяна

СИНТЕТИЧЕСКОЕ МАСЛО

Изобретение относится к составу синтетического смазочного масла, применяемого в области холодильного машиностроения, в частности для смазки холодильных компрессоров, работающих на фреоне-22 до температуры минус 80°С.

Для смазки таких машин применялось обычно нефтяное масло марки ХФ-22 по ГОСТ 5546-59. Смазка нефтяными маслами не может обеспечить нормальную, надежную работу холодильных компрессоров, работающих на фреоне-22 до температуры минус 80°С, поскольку капельки масла ХФ-22, попадая в испарительную часть, затвердевают и забивают систему, снижая возможность получения низких температур порядка минус 70 ÷ минус 80°С.

Предлагается применять в качестве холодильного масла сложные эфиры неопентильных спиртов и жирных кислот C_5 — C_9, которые образуют с фреоном-22 растворы, не застывающие при температуре минус 80°С, так как сами эфиры имеют значительно более высокую точку замерзания, и поэтому могут обеспечить нормальную работу холодильных компрессоров, работающих на фреоне-22.

Предлагаемое синтетическое холодильное масло (марки ЛЗ-ХФ-22С) представляет собой стабилизованный антиокислительным присадками параоксифениламином или ионолом сложный эфир, получаемый при взаимодействии пентаэритрита и синтетических жирных кислот с 5—9 атомами углерода в цепи.

Например (вес. %):

пентаэритритовый эфир	99,5—99,7
параоксидифениламин	0,5—0,3
пентаэритритовый эфир	99,0—99,5
ионол	1,0—0,5

Предмет изобретения

1. Синтетическое масло на основе сложного эфира пентаэритрита и СЖК, *отличающееся* тем, что, с целью обеспечения работоспособности масла в холодильных машинах, работающих на фреоне-22, в него введены синтетические жирные кислоты с 5—9 атомами углерода и антиокислительная присадка.

2. Масло по п. 1, *отличающееся* тем, что в качестве антиокислительной присадки в него введен ионол в количестве 0,5—1,0 вес. % или параоксидифениламин в количестве 0,3—0,5 вес. %.

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Materials Compatibility of R134a in Refrigerant Systems

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Fellow ASHRAE

With the emergence of R134a as a prime candidate and near drop-in substitute for R12, determination of the compatibility of R134a with compressor materials takes on an added urgency. While such work is being conducted in many industrial laboratories, there is no published literature on the subject.

This paper summarizes the work on R134a done in the author's laboratory. Quantitative relations of R134a with lubricants in the form of miscibility diagrams and pressure-temperature solubility are described. The effect of R134a on motor insulation and other materials used in hermetic compressors is explored, and experiences with selected lubricants in compressor and commercial refrigerator-freezer tests are described.

INTRODUCTION

With the ratification by the European Community in mid-December 1988, the Montreal Protocol (UNEP 1987) went into effect on January 1, 1989. What looks like an innocuous first step, i.e., a freeze effective July 1, 1989 on the production of the culpable CFCs at 1986 levels, may turn out to be a reduction of 10% to 15% in the availability of the fully halogenated CFCs. The Hague meeting (UNEP 1988) calls for an accelerated evaluation of the ozone trends, which potentially implies more rapid restrictions on CFCs than agreed upon at Montreal.

These events bring an urgency to find environmentally acceptable substitutes to replace the CFCs. For hermetically sealed systems typified by the domestic refrigerator-freezer, which is the focus of this paper, the clearly emerging substitute for R12 is R134a. After all, its thermodynamic properties are as close to R12 as can be expected; and, being free of chlorine, it is believed to be benign to stratospheric ozone.

The major unknown is the toxicity. However, indications are that the final results will be favorable if one were to judge by the announcements by Du Pont (1988) and ICI (1988)

about plans to spend nearly $100 million for construction of plants to manufacture R134a. Commitment of such funds express confidence not only in favorable toxicity results, but also in the ability of researchers to find solutions to the perceived problems of materials compatibility, especially with the lubricant to be used with R134a in refrigerant systems.

This paper explores the "materials compatibility" problems of R134a, discusses laboratory experimentation regarding "lubricants, motor insulation, polymeric materials and desiccants" and, by way of compressor tests and full-scale refrigerator-freezer tests, hopefully shows that R134a can indeed be a drop-in substitute for R12 in domestic refrigerator-freezers.

COMPATIBILITY WITH LUBRICANTS

R134a has suffered from bad publicity ever since the National Academy of Sciences issued its 1979 report (NAS 1979). In discussing R134a as a substitute for R12 in domestic refrigerator-freezers, the NAS used terms such as "severe electrodeposition of copper: insolubility of oils leading to compressor lubrication problems: mechanical failure: absence of a satisfactory lubricant": etc. These phrases have since then often been repeated, sometimes attributed to the NAS (EPA 1986) and other times paraphrased informally (Braswell 1987). The result is a widespread belief that there are severe impediments to the use of R134a, especially regarding the lubricant. Let us examine these questions.

Conventional Refrigeration Oils

By now, the research community agrees that the currently used refrigeration oils—naphthenic and alkyl benzenes—are just about immiscible with R134a. In practice, what this means is that no matter what proportion of oil and refrigerant one tests, be it 95% R134a or 95% oil, they still remain as two distinct layers regardless of temperature. However, as explained in the ASH-

Table 1

Oil Properties

Oil No.:	1	2
Oil Type:	Polyoxypropylene Glycol	Butyl Monoether
Viscosity 100°F	165 SUS (35.4 cs)	285 SUS (61.7 cs)
210°F	48.6 SUS (6.85 cs)	62.7 (11.0 cs)
Sp Gravity	.983	.989
Flash Point:	316°F (158°C)	341°F (172°C)
Pour Point:	-50°F (-45°C)	-40°F (-40°C)

Oil No.:	3	4
Oil Type:	Polyoxyethylene-Propylene	Glycol Butyl Monoether
Viscosity 100°F	37 cs	110 cs
210°F	7.6 cs	20 cs
Sp Gravity	1.02	1.05
Flash Point:	410°F (210°C)	450°F (232°C)
Pour Point:		-50°F (-45°C)

Oil No.:	5	6	7
Oil Type:	Dibasic Acid Ester	Neopentyl Ester	Neopentyl Ester
Viscosity 100°F	140 SUS	120 SUS	150 SUS
210°F	44 SUS	43 SUS	47 SUS
Sp Gravity	0.91	.998	1.007
Flash Point:	495°F (257°C)	475°F (246°C)	500°F (260°C)
Pour Point:	-70°F (-56°C)	-65°F (-54°C)	-75°F (-59°C)

RAE Handbook (ASHRAE 1986). the two layers are in themselves solutions. each often carrying significant amounts of the other so-called immiscible partner.

In the case of R134a and mineral oil. at room temperature this mutual solubility is less than 1%. but greater than one-tenth of 1%. This mutual solubility. albeit small. can be of crucial importance for oil return in applications such as the domestic refrigerator-freezer.

Glycol-Type Synthetic Oils

The perceived immiscibility and. undoubtedly. the fear that oil would not return from the evaporator. led to the exploration of polyglycols as potential lubricants for use with R134a. The Research Disclosure (DuPont 1978) identified a polyglycol monoether as being miscible with R134a down to SOC and to be chemically stable in sealed tube tests. This oil was tested in a domestic refrigerator-freezer. the teardown analysis of which was described at the Washington Conference on Alternatives to CFCs (Conservation Foundation 1988).

Laboratory data on miscibilities of polyglycols with R134a show that the immiscibility region is not at low temperatures. but at high temperatures. This is opposite of the behavior of R22 or R502 with mineral oils. The concern. therefore. has shifted from the evaporator to the condenser.

Figures 1 and 2 show these inverted domes of phase separation temperatures of polyglycols and R134a. Similar to conventional mineral oil-R22 systems. the higher viscosity polyglycols of the same structure show less miscibility than the lower viscosity grades. As explained in the figure captions. the polyglycols in Figure 1 are polypropylene glycol monoethers. These are also water insoluble. The polyglycols in Figure 2 are also monoethers. but the glycol component is a 50:50 ethylene:propylene structure. This also makes these compounds fully water soluble.

The inverted domes shown in Figures 1 and 2 give the impression that phase separation will occur in the condenser part of a refrigerant system. That is a remote possibility. Even in an automotive system. where the compressor uses pistons with piston rings. the amount of oil circulated is less than 2% by mass of the refrigerant. The phase separation temperature of 98% R134a and 2% oil is considerably higher than the temperature at the bottom of the inverted dome. For example. in Oil 2. which has the appropriate viscosity for an automotive compressor. the phase separation may not occur below 180°F. a condensing temperature which may occur in Arizona summers but not too often. Broad-base immiscibility diagrams like those in Figures 1 and 2 obfuscate these fine points. which are so important for actual applications.
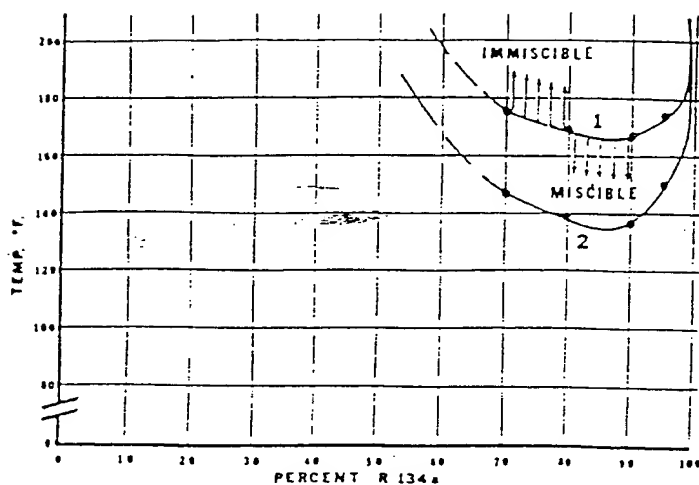
Figure 1 *Miscibility of R134a and Polypropylene Glycol Monoether Oils*
1 - 165 SUS grade
2 - 285 SUS grade
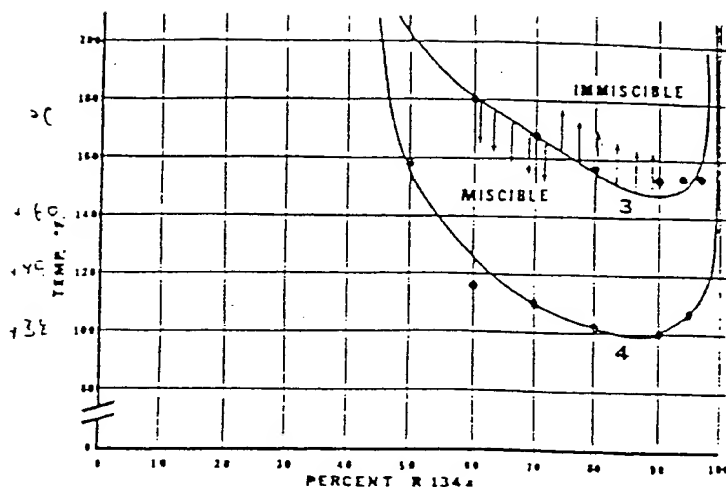
Figure 2 *Miscibility of R134a and Polyethylene-Propylene Glycol Monoether Oils*
3 - 8 cs at 100°C
4 - 20 cs at 100°C

Miscibility data of R134a and polyglycols. other than monoethers. have been described in a recent patent (Magid 1988) and need not be discussed here.

Ester-Type Synthetic Oils

A whole class of synthetic oils of the ester type appears to have adequate miscibility with R134a. Figure 3 shows the miscibility domes for one dibasic acid ester and two neopentyl esters. A casual glance shows that these behave in the conventional manner (similar to R22-mineral oil). However. a faint single point of immiscibility at 80% R134a 20% Oil 7 at +200°F was noticed. Ester formulations should be checked for the high-temperature immiscibility to avoid unforeseen problems. The dibasic acid ester (Oil 5) and the neopentyl ester (Oil 6) are fully formulated. commercially available products. Oil 7 is an experimental oil and is the same oil as described in a previous publication (Sanvordenker 1972). as is Oil 5.

Solubility of R134a in Lubricants

Although miscibility diagrams give an indication of the mutual solubility of the oil and refrigerant. the more important property is the pressure-temperature-solubility relation. The dissolved refrigerant decreases the viscosity of the oil and this property is the determinant for proper lubrication of the compressor and for oil return from the evaporator. The P-T-S diagram for a 165 SUS polypropylene glycol monoether is shown in Figure 4 and a similar plot for a 150 SUS pentaerythritol ester is shown in Figure 5. These data show that the solubilities of R134a in the polyglycol and the ester are somewhat less than those of R12 in mineral oil. but they are still in the same range.
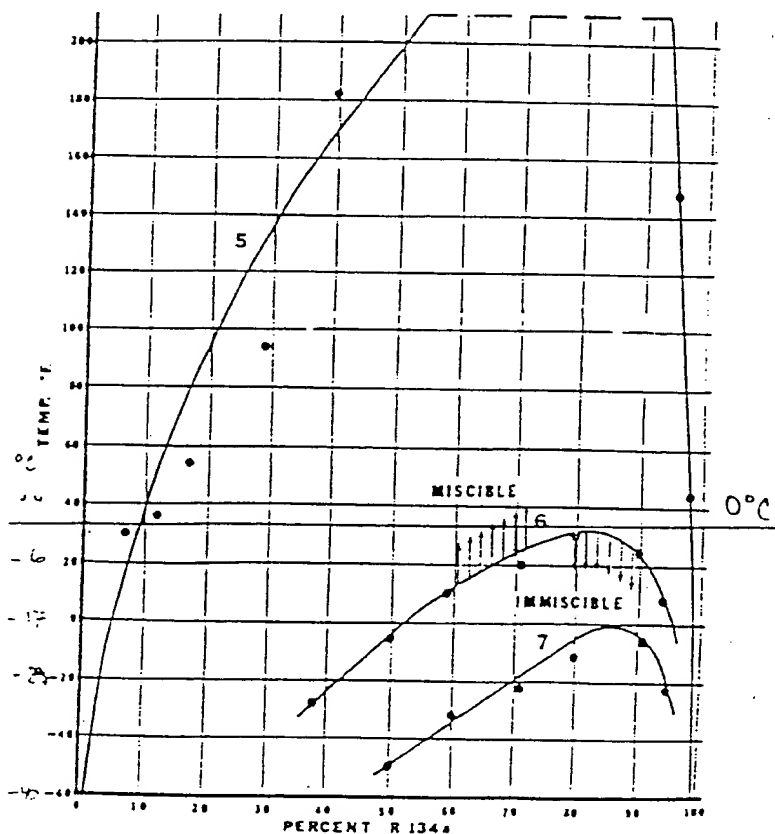
Figure 3 *Miscibility of R134a and Ester-Type Oils VG32*
5 - Dibasic acid ester
6&7- Neopentyl esters

Chemical Reactivity with Lubricants

Using the conventional sealed tube test and with steel and copper as catalysts. R134a appears essentially inert with all kinds of oils. This in-

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Figure 4 Solubility of R134a in Polypropylene Glycol Monoether. 165 SUS at 100°F

Figure 5 Solubility of R134a in Pentaerythritol Ester. 150 SUS at 100°F

des conventional refrigeration oils. the glycol family of oils identified in this paper. as i as the ester-type oils. The horror stories of per plating cited by the NAS in the 1979 report uld appear to be attributable to factors other n R134a-lubricant interactions. A particular ect of stability of some polyglycols needs a ament or two. Some of the glycol-type ricants are prone to deterioration upon ex- ure to air and moisture. ca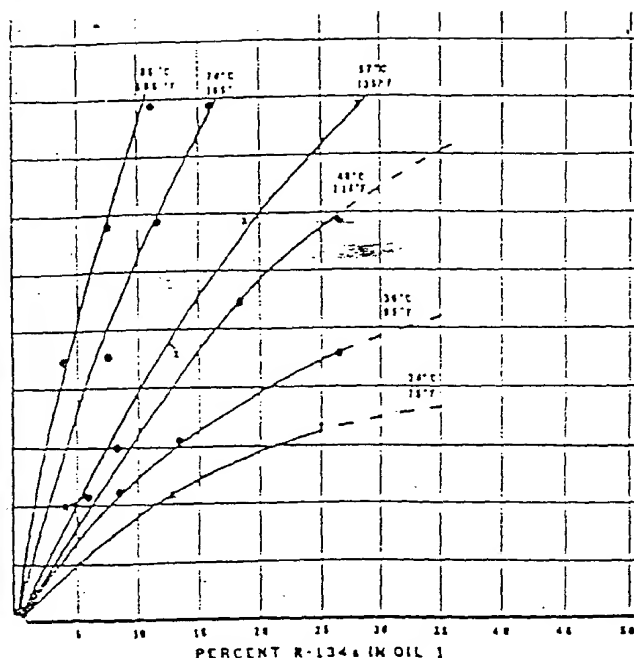using peroxides and lity. Any polyglycol-type lubricants need to be assed under heat and vacuum to remove the oxides and acidic components prior to use in ressors and certainly prior to tests for ity in the laboratory. Carelessness in this ard can lead to erroneous conclusions.

MPATIBILITY WITH MOTOR INSULATION

Magnet wire covering is the primary insulation hermetic motors and it is imperative that this ilation retain its mechanical and electrical in- ity under the refrigerant-lubricant environ- it in which it operates.

R12 has little or no effect on the currently ular magnet wire insulations. It is R22 that cts them. exhibited in the form of softening. tering, and loss of dielectric after thermal ex- sions. A quick gauge of the potential effect of a igerant on motor insulation is to determine the unt of the refrigerant absorbed by the wire mel when fully saturated. This is easily done thermogravimetric analysis. Both polyester ie (PEI) and dual-coat amide imide over

polyester (AI/PE). which absorb approximately 14% R22. absorb a mere 5%-6% of R134a. The difference is significant and may also imply that R134a migrates in and out of the polymers with ease.

Screening tests (Sanvordenker 1971) show that R134a does not soften these insulation sys- tems. does not cause blistering, and has a negli- gible effect on burnout resistance and on the retained dielectric after thermal excursions.

As to the effect of R134a/polyglycol on these insulations. tests were made using twisted pairs in glass sealed tubes containing R134a/polyglycol and compared with R22/mineral oil. Once again. R134a/polyglycol monoether showed no changes in the electrical properties of the PEI or AI/PE. R22/mineral oil degraded the insulations to some degree. as would be expected.

We conclude. therefore. that the magnet wire insulations currently used in hermetic systems are not affected by R134a by itself. nor are they affected by a R134a/polyglycol monoether com- bination.

COMPATIBILITY WITH POLYMERIC MATERIALS

Anaerobic adhesives

Although not too common. anaerobic ad- hesives are sometimes used in hermetic compres- sors in place of mechanical fasteners. If R134a is to be a substitute for R12. then it would be desirable that such adhesives and sealants be compatible with R134a. Two such commercial

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adhesives, sealants were checked: comparisons were made between R12/mineral oil, R22/mineral oil, and R134a/polypropylene glycol monoether. Under parallel test conditions, R134a/glycol affected these materials much like R12/mineral oil, i.e., minimally as compared to R22/mineral oil, which degraded the efficacy of these compounds to some degree.

Elastomers

O-rings made of chloroprene, nitrile, and ethylene propylene rubber were tested for swell in liquid refrigerant. Comparisons were made between R12, R22, and R134a. The dimensional change in R134a was approximately 1.5% for all the elastomers; R22 caused the largest change, approximately 10%, and R12 was intermediate at approximately 5%. Precise dimensional changes vary from one elastomer to another but, suffice it to say, R134a is as benign as R12 toward these common elastomers.

COMPATIBILITY WITH DESICCANTS

The typical R12 hermetic system incorporates a dryer, with Type 4A molecular sieves as the preferred desiccant. R134a systems are also expected to have a dryer, particularly if the lubricant is a polyglycol, which is quite hygroscopic and dissolves large amounts of moisture. R12 has no compatibility problems with Type 4A sieves. But, because R22 tends to react with Type 4A sieves, there is concern over possible reactions of R134a with this efficient desiccant.

For R134a to react with molecular sieves, two things must happen. First, R134a must enter the cavities of the sieves, which have an opening nominally of 4 angstrom units. Second, once there, it must react with the highly alkaline walls of those cavities. R22 does both. With a molecular diameter of less than 4 angstroms, it can enter the 4A sieves and it also reacts readily with alkaline materials.

The molecular diameter of R134a would be 4.26 angstroms, based on an empirical correlation of molecular diameter and the critical properties. Hence, it would be difficult for R134a to enter the 4A sieves. Laboratory experiments with R134a and aqueous sodium hydroxide show no neutralization of the alkali by R134a; by contrast, R22 reacts readily under parallel experiments (Hayashi 1965). Put together, there should be no worry about the compatibility of R134a and Type 4A molecular sieves.

SYSTEM TESTS

The proof of the pudding in this case lies in compressor tests and in full-scale application tests, such as refrigerator-freezer tests. Tests of both types have been made. Details follow.

Compressor Test

The compressor test involves a simple set-up of compressor, condenser, expansion valve, and evaporator. For simulation of a refrigerator-freezer, the suction pressure would correspond to -5°F saturation, and the discharge pressure to +130°F saturation. Test severity is accelerated by operating the system in a high ambient and by adjusting the air movement so as to maintain the temperatures at predetermined levels based on past experience. The key temperature for this test is the temperature in the discharge cavity immediately past the discharge valve.

In comparing R134a with R12, it became necessary to run instrumented compressors under parallel conditions in order to determine the discharge cavity temperature for R12 and R134a. It turns out that both the discharge cavity temperature and the suction cavity temperature are 45°F and 25°F, respectively, lower for R134a than for R12 for the same evaporator and condensing temperatures.

This was to be expected based on the thermodynamic properties of R134a compared to R12. In practice, it meant that the R134a compressor would run somewhat cooler than an R12 compressor. Based on those data, a compressor test using R134a and a polyglycol oil (Oil 1) was conducted for 2000 hours successfully.

The successful result of this life test did not come as a surprise. In a paper published 17 years ago (Sanvordenker 1972) this author reported that polyglycols were used in hermetic compressors to compress inert gases and were found satisfactory even under heavy loading. The test with R134a-polyglycol appeared to confirm that previous experience, in view of the inert behavior of R134a.

Refrigerator-Freezer Test

The compressor test described in the preceding paragraphs was meant to test the durability and reliability of R134a-polyglycol as the working fluid. The refrigerator test was made to confirm the expectation that R134a-conventional mineral oil would be a viable working fluid for this application.

The refrigerator was a commercial 15 ft³, two-door, frost-free, i.e., with a defrost timer and an electric heater, with a wire-on-tube condenser and an auxiliary oil cooler condenser. The compressor was an 800-Btu reciprocating unit made by the author's company. This refrigerator was designed to operate with R12 and had been used for keeping lunches in the author's laboratory.

This refrigerator was operated with no alterations other than a thorough evacuation to remove all remnants of R12 and then charging it with R134a. As mentioned, the oil was a naphthenic oil of 150 SUS grade.

The refrigerator ran like a charm: first, for three days on a temperature control, which meant

an off-on cycling every half hour or so and defrosting every eight hours: second. for a week on a continuous run with a freezer temperature of -5°F, except for a shutdown during defrosting every eight hours: and finally for 10 days on a continuous run without defrost (i.e., with defrost disconnected), and a freezer temperature of -5° to -7°F.

At the end of this time period the test was terminated. The objective of the test—which was to confirm that oil return would not be a problem with R134a and mineral oil in a domestic refrigerator-freezer—was met satisfactorily.

As to the explanation why, it must be recognized that these reciprocating hermetic compressors pump very little oil, typically less than 1/4 oz per hour. Based on the refrigerant pumping rate, this may mean an oil-to-refrigerant ratio on the order of 0.2% to 0.1%. The mutual solubility of mineral oil in R134a is in that vicinity, which is one important factor, the other being that mineral oils have a degree of fluidity even at -20°F in the presence of R134a.

SUMMARY

This paper brings into the public domain a large body of information developed in the author's laboratory regarding the interactions of R134a with materials in refrigerant systems. Factual data on miscibilities of R134a and several potential lubricants are presented. Solubilities of R134a as a function of temperature and pressure for two lubricant systems are also presented. R134a, even in combination with a supposedly aggressive lubricant like a polyglycol, is shown to be as benign as R12/mineral oil toward magnet wire insulation, anaerobic adhesives, and elastomeric materials. Methods to evaluate interactions with desiccants based on elementary logic and minimal experimentation are explained.

In addition, system tests using a commercial refrigerator-freezer designed for R12/mineral oil were made replacing R12 with R134a without any

other changes. The refrigerator/freezer worked like a charm, including a 10-day continuous run without defrost, which in reality is a simulation of a chest freezer.

As a final word . . . while agreeing that one swallow does not a summer make . . . it is still an interesting speculation that if R12 were not available. refrigerator-freezers would be quite functional with R134a as a drop-in, assuming, of course. that such appliances would be equipped with a compressor similar to the one used in this particular test.

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speculate on how these could influence an aluminum reaction.

Filter-dryers are commonly used which remove acid as well as the oil polymerization products formed from the reaction shown in Eq (1). As long as these are effective in preventing a build-up of degradation products, the chemical environment conducive to an aluminum reaction should not form, even when the R12/oil stability is insufficient.

In a system with aluminum moving parts, the protective aluminum oxide can be removed by abrasion. We are told that it is not uncommon to find fine aluminum particles among the sludge in used compressors with aluminum bearings, indicating that free aluminum was exposed to the refrigerant-oil mixture at some time. The combination of abrasion and a corrosive environment should permit an aluminum reaction to occur under more moderate conditions than those required in our static tests.

Small quantities of air and water are often present in real systems. These, or other sources of oxygen, would re-oxidize bare aluminum surfaces and thus tend to prevent an aluminum reaction.

SUMMARY

1. action between aluminum and Refrigerant 12 and oil was reproducibly initiated by heating the combined materials at temperatures of 300F and higher. Before the reaction would start, however, the R12/oil fluid had to be degraded to the extent that it was black and contained a high level of acid. It is believed that this black corrosive fluid partially removes the protective oxide from the aluminum, permitting direct contact and reaction with the refrigerant.

2. The initial reaction that occurred was the combination of aluminum with refrigerant to produce aluminum halides and carbonaceous matter. Once this had started, secondary reactions began. At 300F the secondary reaction is decomposition of Refrigerant 12 to produce

Refrigerant-13 is a stable product. At 400F oil cracking occurred, producing a mixture of light hydrocarbons and coke-like matter. These secondary reactions are believed to be catalyzed by the aluminum halide formed from the refrigerant-aluminum reaction, which would account for the fact that they occur only subsequent to the latter reaction. No evidence for a direct reaction between aluminum and oil was found. The final end products were aluminum halides, coke, gaseous oil-cracking products or R13.

3. A precondition for the aluminum reaction is the severe degradation of the refrigerant-oil mixture. It is concluded, therefore, that in the tests reported here overall stability was limited by the stability of the refrigerant-oil mixture and not by the aluminum.

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A REVIEW OF SYNTHETIC OILS FOR REFRIGERATION USE

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The infatuation of refrigeration engineers with synthetic oils dates back to 1929, when the first synthetic oil was commercially manufactured and was thought to be ideal for ice making equipment.[1] Fifteen years later the polyglycols were considered for the same application.[2] The mid-fifties saw the alkylbenzenes,[3] which only now are in limited use in Europe, and a silicate ester[4,5] which was tested in systems but has been abandoned. The sixties saw a proliferation of synthetic materials developed for military jet aircraft. Some of these have also been examined but none were used for refrigeration. The situation is like that of a car buyer who closely examines flashy sports cars but eventually decides to by a four door sedan.

Admittedly, synthetic oils were considered because of

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specific problems with mineral oils, for example, wax separation and low miscibility with some refrigerants. Although these drawbacks still exist, improvements in petroleum processing and system design have extended the useful low temperature limit of mineral oils. Combined with the economics involved, this has effectively kept synthetic oils from large scale use in refrigeration.

There are two reasons for the renewed interest in synthetics. Publicly stated is the need of easier oil return from low temperature evaporators. Privately, carbonization of valves is mentioned as an equally serious problem. Many people feel that these problems may be solved by synthetic oil technology. Furthermore, because only a limited segment of the industry requires oils for low temperature application, there is a willingness to pay a premium price. A survey of the capabilities and limitations of the various synthetic oils is therefore timely and is the subject of this paper.

COMPLEXITIES OF DESCRIBING SYNTHETICS

Today the refrigeration engineer can predict the general behavior of mineral oils from a few key properties largely because of his familiarity with them. The same does not hold true for synthetics. Not only do they include lubricants of diverse chemical classes, but even within the same class the properties may vary in an unpredictable fashion. Occasionally the traditional means of comparing properties may even become meaningless. A good example is the viscosity index (VI). 2-ethyl-hexyl disiloxane has a VI of 230 whereas the equivalent trisiloxane has a VI of 178. However, the viscosity of the latter is less affected by temperature; i.e., the opposite of what the VI would indicate.[6] Another example can be seen with two dibasic acid esters; i.e., Di (3-methyl-butyl) adipate and Di (1-methyl-ethyl) sebacate. Both have essentially an identical density, viscosity grade, viscosity index, molecular weight and number of chain units. Yet one freezes at +32F and the other at −44F.[7]

The refrigeration engineer must also recognize that most of the literature on synthetic oils is directed at the aerospace engineer, with test methods, acceptance criteria or specifications all reflecting this fact. One often reads, for example, of jet aircraft fluids with a capability of lubricating from −65 to +400F. This does not mean that the crankcase operates at −65F; it simply means that the aircraft can be started when at rest in a −65F ambient, and a viscosity of about 14,000 cs is considered acceptable for this purpose. The upper temperature capability is defined by another specification on viscosity; i.e., 1 cs at 400F (MIL L-9236B). A new material which maintains a viscosity of 1 cs at, say, 500F, may be described as having a lubricating capability of 500F.

Once this new frame of reference is accepted, discussing synthetics becomes a simple problem.

EXPLOITING THE PROPERTIES OF SYNTHETIC OILS

Except by accident, one can rarely obtain the full advantage of a new material by simple substitution, rather it must be engineered into the system. Let us consider two such situations:

a. Viscosity Temperature Relations: Many refrigerant compressors today use a 150 viscosity grade oil, i.e., 150 SUS at 100F. During operation, the compressor runs hotter than 100F, and the oil entering the bearings may well be over 200F. In other words, these compressors are designed for lubrication by the present mineral oils which, at 210F have a typical viscosity of 44 SUS or 4.5 cs. In selecting a synthetic oil, emphasis should be placed more on the viscosity at 210F and less on the value at 100F. For example, the 150 SUS neopentyl ester in Table I has a viscosity of 6.5 cs at 210F. This viscosity may be higher than needed for lubrication and sealing and may even cause more friction. The proper choice would be a 75 SUS grade, which may be perfectly adequate. The advantage would also lie in a somewhat lower pour point of 75 SUS grade.

b. Miscibility With Refrigerants. It is well recognized that oil return from evaporators is easier when the oil is miscible with the refrigerant. Many of the synthetics remain miscible with R22 and R502 even at very low temperatures. However, the real criterion of fluidity lies in the pressure-temperature-solubility relations of the oil-refrigerant system. Such data must be carefully determined for the synthetics if the miscibility advantages are to be fully exploited.

COMPARISON OF PROPERTIES

The properties of most of the commercially available synthetics are compiled in Table I to illustrate their relevant refrigeration characteristics. Except for silicate esters, these properties are derived from samples checked in the authors' laboratories. Some data are self-explanatory, others are not. The low temperature fluidity, for example, is either the temperature at which the oil phase coagulates (after phase separation) or in case of complete miscibility, it is the temperature at which a 1:3 mixture of R22 oil ceases to flow. The excellent chemical stability noted in some cases was obtained only for one of the several additive formulations and in that sense is really work on the additives. The experience factor implies that these oils have been tested in compressors by sources known to the authors. The potential suppliers are given as a lead and not as sources of a particular sample. Costs are approximate and not quotations.

1 Synthetic Hydrocarbons

a Paraffinic. This was the first commercially marketed synthetic oil, and was a major advance by the standards of the time (1929). Standard Oil Company of Indiana produced about three million gallons before the operation was abandoned.[1] Structurally the oil consisted of branched chain, saturated paraffins, similar to some components of refrigeration oil. It contained no wax, had a high Viscosity Index, excellent color stability and low carbon forming tendency.[3] Interestingly, the same factors which influence new product failure today, caused the demise of this material then; since all synthetics are at least partially based on petrochemicals, the product was more expensive than,

TABLE 1

COMPARISON OF PROPERTIES OF MINERALS AND SYNTHETIC OILS

CLASSIFICATION	MINERAL OIL	PARAFFINIC HYDRO-CARBONS	ALKYL-BENZENES	DIBASIC ACID ESTERS	POLY GLYCOLS[1]	SILICATE ESTERS[2]	PHOS-PHATE ESTERS (TCP)	FLUORO-CARBON OILS	NEOPENTYL ESTERS	SILICONES
Viscosity @ 100 F SUS	155	150	153	140	102	151	164	119	150	55
Viscosity @ 210 F SUS	41	45	39	42	44	63	41	36	48	48
Viscosity @ 210 F Cs	4.5	5.7	3.9	5.4	5.3	11.3	4.4	3.0	6.5	6.5
Viscosity Index	0	135	<0	132	180	178	<0	<0	117	230
Pour Point F	-45	-65	-40	-75	-65	<-100	-15	-40	-70	-85
Flash Point F	340	455	340	490	420	395	405	---	550	---
Additives	none	yes	none	yes	yes	yes	none	none	yes	yes
R12 Chemical Stability	excellent	excellent	excellent	good	good	---	very poor	excellent	excellent	excellent
Low Temperature Properties										
Phase Separation F, 80% R22, 20% oil	30	>140	-100	<-100	-100[3]	-100[5]	<-100	-100	<-100	-100
Phase Separation F, 80% R502, 20% oil	180	---	5	-90	<-50[3]	---	<-70	<-112	<-100	<-65
Low Temperature Fluidity, F[4]	-75	-75	-95	<-100	-80[3]	---	---	<-100	<-100	<-100
Effect On Elastomers	slight	none	some	some soften-ing	none	---	swells & plastici-zes	none	---	possible extraction & shrinkage
Lubricity	good	good	fair	good	good	good to fair	excellent	excellent	good	fair to poor
Cost $/Gallon	0.50-3.00	3.00-4.00	1.50-2.00	4.00-8.00	2.00-6.00	10.00-30.00	3.00-4.00	200.00	6.00-8.00	20.00-40.00
Experience Factor	excellent	small	good	none	some	some	---	none	none	---
Potential Sources of Supply	Sun Oil Co Texaco	Mobil Shell Humble	Shell Humble Chevron	Union Carbide Monsanto Tenneco	Dow Union Carbide	Monsanto Union Carbide Chevron	Celanese Monsanto E F Houghton	Hooker 3M Halo-carbon ProdCorp	Tenneco Ultrachem Celanese	Dow Corning Union Carbide G.I.

1. Reference 16
2. Reference 22
3. Data on a monoether
4. See Text
5. Expected behavior

(6

the mineral oils. The other factor was the technical improvement in mineral oils. Petroleum refiners developed VI improvers which effectively undercut the technical advantage of the synthetic paraffins.

Today, several oil companies manufacture synthetic paraffins for hydraulic fluids, and also in viscosity grades for lubrication. The present products are far superior in viscosity-temperature relations, with oxidation inhibitors and lubricity additives, they become excellent refrigeration oils. The only drawback is their poor miscibility with R22. However, when the low temperature fluidity of the oil phase (with R22) is considered, these oils seem to remain fluid to the same temperature levels as the current refrigeration oils; with R12 system tests in high ambients, they appear to be superior to present mineral oils and do not show valve deposits.

b. Alkyl Benzenes. Just as the synthetic paraffins are similar to the saturated components of mineral oils, the alkylbenzenes are the cousins of the aromatic components. A major advantage of these materials is their excellent ability with R22 and R502. With R502, although phase separation occurs at 0 degree to 10F, the oil phase remains fluid down to −90F. With R22, they remain miscible below −100F.

These oils have been described in ASHRAE literature,[9] and are currently used to a limited extent in Europe. One of their drawbacks is the low viscosity index, which can cause thinning of the oil at high crankcase temperatures. Increase in the alkyl chains improves the viscosity index, but causes some loss in the R22 miscibility. There is also some confusion on the behavior of such oils. Seeman and Shellard[10] find that they have poor lubricity and recommend addition of mineral oil to improve it. Steinle,[11] on the other hand, finds the lubricity satisfactory and reports that they also have good resistance to coking. However, when tested in an R12 system at high ambients, we found valve deposits with the German oil.

An interesting speculation on the synthetic hydrocarbons is the possibility of blending the alkyl benzenes with synthetic paraffins. Such blends would incorporate the temperature properties of the paraffins and low temperature properties of the alkyl benzenes, and the mixtures would resemble the mineral oils with which we are so familiar.

2. Dibasic Acid Esters

The annual production alone of these materials, which is 3 to 4 million gallons, puts them into one of the more important classes of synthetic oils. They have excellent viscosity-temperature relations, low pour points and good thermal stability (according to military requirements). Also, extensive work has been done on the correlations of properties with structure. We refer the reader to Duiek & Poppin[12] for an excellent summary of the properties of the diesters and their historic development.

Structurally, a dibasic acid is one which contains two carboxylic acid groups. When reacted with two alcohol molecules, the dibasic acid ester results. Quite unlike

mineral oils, these are polar compounds containing two carbonyl groups.

Being polar compounds, they can be expected to be more reactive with refrigerants than mineral oils. Also, the reactivity has to be measured on the basis of CO_2 evolved in addition to the R22 formed. However, we have found materials (containing additives) which are quite stable in sealed tube tests. The non-additive samples showed high reactivity.

The dibasic acid esters also seem to be miscible with R22 and R502. The sample shown in Table I indicates no phase separation with R22 even at −100F. However, being a chemical compound each formulation must be checked for this property.

Although the above are very desirable characteristics, some cautionary notes are in order. The diesters can have a significant effect on elastomers (one of their commercial applications is as plasticizers). Since there is a possibility that head gaskets in a compressor may blow off, each compound needs to be checked for that. A second consideration is their pour point. Being pure compounds, they should have a freezing point rather than a pour point. But it is possible for the diesters to supercool and temporarily remain liquid below their freezing point, and then freeze after being left at that temperature for some time. For this reason, the low temperature fluidity must be evaluated with caution. To explain this further, we find that the ester in Table I remains fluid at −100F, when containing 25% R22. This may indeed be an intrinsic property, but it may also have been affected by supercooling, and needs to be investigated further. Finally, with esters there is the possibility of hydrolysis. This problem is aggravated by contamination of a diester from low molecular weight materials. With mineral oils, contamination by light ends is rarely a problem. It may show up in a lower flash point but it does not affect the chemical stability. With dibasic esters, as with any esters, the low molecular weight materials are chemically less stable and their decomposition products act as reaction catalysts, even if the basic bulk material is stable.

These are not major problems, but are presented as cautionary notes. All together, these esters have a potential as low temperature refrigeration oils, certainly with R22 to −70F, and possibly to the −100F range.

3. Neopentyl Esters

These compounds represent a further development, having all the advantageous properties of dibasic acid esters, and, in addition having a higher thermal and oxidative stability. They are based on specific polyols with the five carbon neopentane structure, the most important of which is pentaerythritol. This carbon structure is considered to be the key to the high temperature stability.[13]

Properties of a neopentyl ester relevant to refrigeration appear to be very close to those of the dibasic acid ester shown in Table I. Although the higher thermal and oxidative stability is indeed a plus factor, this added capability may not be required for refrigeration purposes. The low temperature characteristics are close to those of

dibasic acid esters, and hence the neopentyl esters do not appear to offer any major advantages for refrigeration which would justify their higher cost. A recent Russian patent[14], however, does mention a pentaerythritol ester as a lubricant with R22, to be used for evaporator temperatures of −80C (−112F)

4. Phosphate Esters

The refrigeration industry is quite familiar with at least one phosphate ester, viz. tricresyl phosphate, which is often used as a lubricity additive to refrigeration oils.

Except as additives, the phosphate esters have little to offer. Their viscosity-temperature relations are in the same range as mineral oils. An exception is n-hexadecyl diphenyl phosphate, having a viscosity index of 162, and falling in the 100 SUS viscosity grade.[15] This is of no value, because its pour point is +45F. Others have low pour points, but their viscosities are too low. But the high temperature properties are the most worrisome of all. The phosphate esters decompose to form substituted phosphonic acids and even the more stable ones are just not suitable at normal temperatures. Thus, phosphate esters can be eliminated on technical grounds alone.

5. Polyglycols

These materials should properly be called ethers and esters rather than glycols because the terminal hydroxyl groups are bound by ester or ether groups. This substitution makes the polyglycols suitable for lubrication and also renders them water insoluble. When first introduced in 1946, they were mentioned as potential refrigeration oils.[2]

The polyglycol lubricants have excellent viscosity temperature relations. A 100 SUS grade diether, for example, has a higher viscosity at 210 deg than a 150 SUS grade mineral oil.[16] Perhaps a more significant property of the polyglycols is that they cool down to their pour point by a steady increase in viscosity, much as the naphthenic mineral oils do. This should permit the use of polyglycols to temperatures much lower than their pour points, since they are also miscible with R22 and R502.

In the laboratory, a 165 SUS grade monoether showed a pour point of about −55F. Mixed with 25% R22 it yielded a fluid to about −80F, and a 1:1 mixture was still fluid below −110F. The diethers should be much better.

The polyglycols have been used in hermetic compressors with inert gases and have been found to be quite satisfactory even under heavy compressor loading. Hence, we consider them to be good lubricants, and to have good electrical insulating properties. Moreover, this experience also indicates that they have little or no effect on normal elastomeric materials used in hermetic compressors.

In sealed tube tests, a monoether with proper additives was found to have very good stability with R12. The polyglycols are also supposed to be slightly hygroscopic but this would not be a major drawback for refrigeration purposes. The only other item is that the monoethers show immiscibility curves with mineral oils similar to those found for R22 and mineral oils.[17] The diethers are supposed to be completely miscible.

All properties considered, the polyglycols appear promising as refrigeration oils and deserve much more attention than they have received so far.

6 Silicate Esters and Silicones

As the name suggests, both are based on silicon chemistry. The basic difference is that for the silicate esters, the silicon atom would be attached to the substitution group only through an oxygen atom. For engineering purposes it is enough to say that the silicones derive their primary properties from the long chain of silicon atoms, whereas the silicate esters depend on the long substitution chains.

a. Silicate Esters: Among the various synthetics, the silicate esters appear to have the lowest pour points. In examining the properties of the orthosilicates and disiloxanes, one cannot help noticing the "<" sign prefixing the already low pour points.[16] Equally striking are their excellent viscosity temperature relations.[6]

One silicate ester, identified as a "secondary butyl ester of polysilicic acid" has been described by Steinle[4] and by Loffler[5] in German refrigeration literature, and its viscosity data with R13 have been published in ASHRAE literature.[9,19] This German formulation has been commercially tested[20] and abandoned because of breakdown even at moderate operating temperatures.

Unfortunately, this experience is based only on one formulation, which gained prominence because the German researchers were the first to recognize the miscibility relations of the silicate esters with polar refrigerants. Perhaps less known is the fact that extensive work on silicate esters was being done in this country at about the same time.[21] As a result, stable disiloxanes have long been available in this country. Detailed data on two such fluids have been published by Furby et al.[22]

Because of the experience with the German formulation, it seems worthwhile to review Furby's test data on the fluid 8200, which is based on hexa (2-ethyl butoxy) disiloxane.[23] The material showed no change in viscosity and formed no insolubles in the hydrolytic stability test (MIL H-8446). Even after 336 hours with water and copper catalyst, the only deterioration was a 6% increase in viscosity. In an oxidation test in presence of metal catalysts, even after 72 hours at 400F, no insolubles were formed and the only change was that the viscosity measured at 210F dropped from 11 cs to 9 cs. In an inert atmosphere, the fluid showed no change under otherwise similar conditions. Tests in hydraulic pumps at temperatures up to 400F for 20 hours showed no problems. The formulation was also of a reasonable viscosity range (11 cst at 210F).

We should hasten to point out that we have not made any laboratory or compressor tests with such materials. Nevertheless, the published data indicate that the problems of silicate esters, i.e. thermal, hydrolytic and oxidative stabilities may be minimal with the above formulations. Other information on the effect of structure on hydrolytic stability[13] and on viscosity-temperature relations[5] has also been published. Such materials therefore deserve reconsid-

eration for low temperature refrigeration usage in spite of the problems cited by Downing and Cooper[20]

b *Silicones:* Like silicate esters, the silicones are miscible with R22, but their pour points are somewhat higher. The silicones also have good viscosity temperature relations, but associated with these is a limited solvent power for additives. The solvent power can be improved by incorporating aromatic side chains, but this causes some loss in viscosity index as well as in pour point. Silicones are considered only fair lubricants, but this property is improved by small additions of fluorocarbon oils. Overall, the good chemical stability and miscibility with refrigerants do make silicones potential refrigeration oils. However, their slightly higher cost and higher pour points compared to silicate esters may be a deterrent.

7. Fluorochlorocarbons and Fluorosilicones

a. *Fluorocarbon Polymers:* The fluorocarbon polymers belong to the same chemical family as the halocarbon refrigerants and are naturally compatible with each other. They are also good lubricants and are thermally and chemically stable.[24] Only their viscosity-temperature relations are poor. But the real drawback is their cost - $200/gallon. At this price the interest in fluorocarbon lubricants fades very rapidly.

b. *Fluorinated Silicones:* Replacement of the hydrogen by fluorine in silicones sharply improves their thermal stability, lubricity and resistance to acids. However, similar to fluorocarbon polymers, the cost rockets to the $200/gallon range.

SUMMARY

Most of todays commercially available classes of synthetic oils are described in this article. Among these, only the phosphate esters seem unsuitable for refrigeration use. Except for the synthetic paraffins, all others are miscible with R22 to very low temperatures. In each case, using additive technology, excellent stability with refrigerants is possible, and has been so demonstrated. Since cost is a crucial factor in the selection of any oil, it appears that the alkylbenzenes, the polyglycols, the dibasic acid esters and the silicate esters are the most attractive candidates for low temperature applications. With careful evaluation and predefinition of the product, the synthetics, including the paraffins, technically have much to offer. The cost effectiveness, however, has to be left to the individual systems designer.

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